Some Electrical and Chemical Effects of the Explosion of Azoimide.

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Introduction.—In a paper* published some years ago, the amount of electricity liberated by exploding electrolytic gas $(2H_2 + O_2)$ at certain pressures was measured and compared with the number of molecules of water formed by the explosion. It was found that about 10^7 molecules of water were formed for every pair of gaseous ions that reached the electrodes, and that the energy required to produce the observed quantity of electricity was an extremely small fraction of the energy set free by the explosion.

The present investigation was undertaken to see whether these results would be substantially modified in the case of the explosion of azoimide (HN_3). The explosion of this gas differs from that of electrolytic gas in two important particulars from the point of view of these experiments. In the first place it is disruptive, and secondly it is not productive of water-vapour, which with its well-known influence upon the motion of gaseous ions may, by promoting their re-combination, greatly obscure the electrical effects of the explosion.

Method of Research.—The method consisted in exploding the gas at various low pressures between two electrodes charged to a potential difference and in measuring the quantity of electricity thrown on to one of the electrodes. Then, the volume of the gas contained between the electrodes being known, and its pressure, it is easy to find the ratio between the number of pairs of gaseous ions that find their way to the electrodes and the total number of molecules of the gas disrupted.

Preparation of the Azoimide.—The gas was generated by admitting dilute sulphuric acid into an exhausted vessel containing barium azoimide. The latter (BaN_6) was prepared in the following way. Nitrous oxide was passed over sodamide at the temperature 190° C. The product of this reaction was dissolved by water, and excess of sulphuric acid was added to it. From this solution the azoimide was distilled into barium hydroxide, forming barium azoimide, the excess of barium hydroxide was precipitated by carbon dioxide, and the solution after filtering was evaporated to dryness. The residue was redissolved in water to remove a small amount of carbonate, and on evaporation the pure salt was obtained, which after drying was analysed;

* C. E. Haselfoot and P. J. Kirkby, ' Phil. Mag.,' October, 1904.

0·9294 grm. of the salt gave 0·9688 grm. of $BaSO_4$, from which numbers the percentage of barium was found to be 61·3 (calc. BaN_6 61·9).

Description of the Apparatus.—The salt (BaN_6) having been thus prepared, about a gramme was placed in a small vessel C, illustrated in fig. 1, which shows the apparatus in diagrammatic form.   E is a drying vessel containing calcium chloride, G is a vessel for receiving the gas and I is a U-tube manometer, which when the tap J was opened was in connection with the little explosion chamber S.   The tube T was connected with a Fleuss oil-pump.   To generate the gas, normal solution of sulphuric acid in excess of the salt in C was placed in the funnel A, and with all the taps open except B
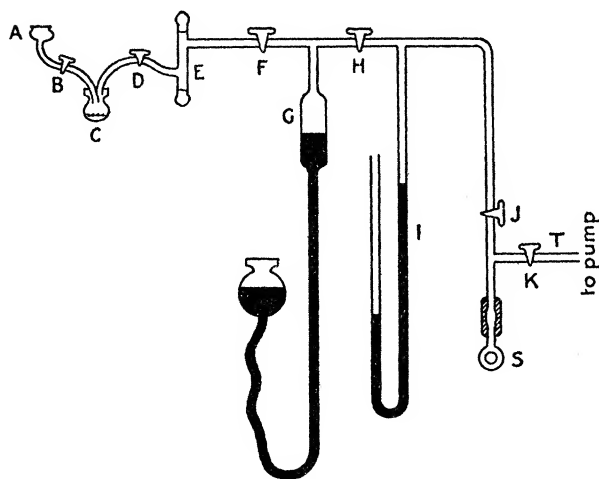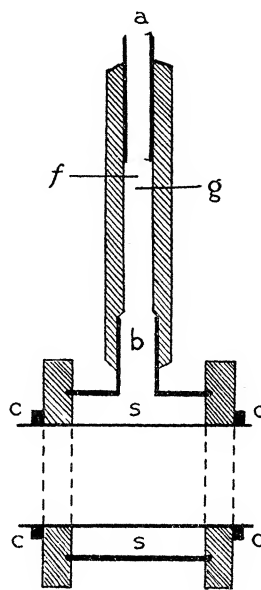

FIG. 1.   FIG. 2.

the air in C was pumped out; D was then closed and the sulphuric acid admitted through B, and the reaction having been accelerated by surrounding C with hot water, the gas produced was dried in E, collected in G and sometimes pressed back into E for further drying.   Before an experiment S was exhausted by the pump and azoimide admitted and then immediately exploded.   The object of the tap J was to economise the gas.

The explosion chamber S, which consisted principally of two co-axial cylinders separated by ebonite, is illustrated in fig. 2, drawn to scale, which represents a section of it by a plane through the axis of the cylinders.   The shaded parts of the diagram represent ebonite: *a* is the end of a glass tube leading to the apparatus just described, *b* is a brass tube leading to the

space *s* between the co-axial cylinders.   These cylinders, which were of gilded brass, were insulated from one another by means of two blocks of ebonite, through which the inner cylinder passed, the brass rings *c, d,* serving merely to prevent the ebonite from being displaced by the explosion.   The spark-gap is between the thick aluminium wires *f* and *g,* which are fixed in an ebonite sleeve fitting the tubes *a, b,* accurately.   All the joints were made with black elastic glue.

The outer diameter of the inner tube was 2·23 cm., and the inner diameter of the outer tube was 3·33.   The length of the outer tube was 3·02 cm. Hence the volume between the electrodes was 14·5 c.c.

Electrical Arrangements.—These were very simple.   The outer cylinder was connected to one of the Oxford City mains (voltage about 105), and the inner through a low resistance ballistic D'Arsonval galvanometer to the other main.   The spark-gap terminals *f* and *g* were connected to the ends of a small induction coil.

Method of Experiment.—The explosion chamber was exhausted by the oil pump to as low a pressure as possible.   (The " vacuum " attained was about 2 mm. or less, most of the residual pressure being most probably due to water-vapour.)   Then the gas was admitted from the adjoining chamber and exploded, and the resulting throw of the galvanometer determined.   It was verified that no part of the throw was due to the sparking.

Results.—The results of three series of experiments are given in the following tables, a " series " being a number of experiments carried out continuously in the order given upon the same sample of gas.   In every case recorded in the tables the difference of potential of the cylinders was nearly 105 volts.

Notation of the Tables.—

p = the pressure of the gas in millimetres of mercury.

Q = the observed quantity of electricity in micro-coulombs.

μ = the number of molecules of gas exploded divided by the number of pairs of ions that reach the electrodes.

(It is easy to prove that $\mu = 7\cdot8 \times 10^4 p/Q$ by means of the well-known equation $Ne = 1\cdot22 \times 10^{10}$, where N is the number of molecules of a gas in 1 c.c. at 760 mm. pressure and 15° temperature, and e is the charge on an electron in electrostatic units; for the volume of gas exploded between the electrodes was 14·5 c.c.)

Previous to the series of experiments in Table I the gas had been dried (in the vessel E of fig. 1) by contact with calcium chloride for 24 hours. The first explosion at the pressure 151 mm. produced much more electricity

Table I.

p.	Q.	$\mu \times 10^{-5}$.	Outer cylinder.
151	69·5	1·69	+
117	11·0	8·3	+
151	10·5	11·2	+
108	11·0	7·7	—
55	6·3	6·8	—
39	4·7	6·5	—
28	4·7	4·6	—
19	5·9	2·5	—
15	4·9	2·4	—
10	No explosion		—

than the rest, and seven times the amount produced by the third explosion under apparently the same conditions. It is impossible to attribute this to any extra dryness; it is an instance of a curious phenomenon repeatedly observed, consisting in the production, not necessarily at the first explosion, of an abnormal amount of electricity for no apparent reason. Each of the three tables given shows an instance of it.* Thus in Table II at the pressure 82 mm. the value of Q is 59, and in Table III, pressure 214 mm., the value of Q is 87. In both these latter cases the throw of the galvanometer was so large that only a rough estimate, noted as less than the true value, was possible.

Table II gives another series of experiments upon azoimide after it had been allowed to remain a few minutes over phosphorus pentoxide in a little

Table II.

p.	Q.	$\mu \times 10^{-5}$.	Outer cylinder.
12·0	No explosion		—
40·0	6·0	5·2	—
82·0	59·0	1·1	—
30·5	7·6	3·1	—
20·0	5·9	2·6	—
13·0	5·0	2·0	—
8·5	No explosion		—
65·5	7·6	6·7	+
40·5	3·7	8·5	+
25·0	2·5	7·8	+
16·0	1·9	6·6	+
11·0	1·2	7·1	+
8·0	No explosion		+

* The same effect was observed in the explosion of $2H_2+O_2$ (*loc. cit.*), and though this was thought to be due to a higher degree of dryness, yet prolonged attempts to dry the gas wholly failed even approximately to reproduce the greater quantities of electricity observed.

vessel between the taps H and J, so that it was probably drier on explosion than in other cases. It is clear though, by comparing Table II with Table I, that this additional drying made no perceptible difference.

The observations recorded in Table II made with outer cylinder positive exhibit a rough constancy in μ (7×10^5 or 8×10^5), independent of the pressure. This table also appears to show that at the lower pressures more electricity resulted from an explosion when the outer cylinder was negative than when it was positive. This latter conclusion is also supported by Table I, in which the values of μ, when the outer cylinder was negative descend from 6.8×10^5 ($p = 55$) to 2.4 ($p = 15$), which last agrees with the values of μ in Table II corresponding to a negative outer cylinder.

It does not seem possible to account for this conclusion by means of any known effects. If the pressure were lower and the inner cylinder much smaller it would be easy to do so. For in that case, if the inner cylinder were positive, the negative ions in moving towards it would pass through the intense field of force surrounding it and so would generate others by collision; whereas, if the inner cylinder were negative, the positive ions in passing through the similarly intense field would produce no appreciable similar effect.* In the present case, however, the field of force was of the same order of intensity between the cylinders. Its value at the inner cylinder was 236 volts per centimetre, and at the outer 186. Now, for a given ratio of electric force to pressure, the number of ions generated by the collisions of an electron per centimetre of its motion is proportional to the pressure of the gas.† It is clear, therefore, that if the increase in the values of Q at the lower pressures, when the outer cylinder was negative, were due to collision effects, aggravated by the abnormal condition of the gas, an increase of the same order would have been observed at the lowest pressures with a positive outer cylinder. In fact, in some cases the ratio of electric force to pressure near the outer cylinder, when that cylinder was positive and no increase in the value of Q was observed, exceeded the same ratio near the inner cylinder when, the inner cylinder being positive, a striking increase was observed. (See Table II, pressures 20, 11, where the ratio in question, applying to the region close to the positive electrode, through which all negative ions had to pass, was 12 and 17 *q.p.*)

Effect of Introducing a Resistance.—The effect of introducing a resistance between one end of a battery and one of the cylinders is shown in Table III.

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* J. S. Townsend, 'Ionisation of Gases by Collision,' p. 11 f. ; or P. J. Kirkby, 'Phil. Mag.,' February, 1902.

† Townsend, *ibid.*, p. 18.

Table III.

(Outer cylinder connected through resistance R to the positive pole.)

p.	Q.	R.	$\mu \times 10^{-5}$.
		ohms.	
124	2·2	10^5	44·0
63	2·9	10^4	17·0
43	0·7	10^5	48·0
30	2·5	0	9·3
214	87·0	0	1·9
152	12·3	0	9·6
217	27·2	0	6·3

The effect is very marked. The explanation is, probably, that the electric force between the cylinders is reduced to such an extent during the passage of the current, when there is a considerable resistance, that the amount of recombination of ions is greatly increased, and the quantity of electricity that reaches the electrodes thereby greatly diminished. In fact, the difference of potential of the electrodes is diminished by CR volts when the current C ampères is flowing; and it is not difficult to show that CR approximated to the voltage V of the battery, *i.e.* the voltage difference of the cylinders when no current was passing. To show this, let us suppose that the quantity Q (micro-coulombs) observed was carried in time t by a stream of ions of constant density and constant velocity u to one electrode. Then, if d denotes the distance between the electrodes, $t = d/u$ and $C = Q \times 10^{-6} u/d$. Now, the electric force under which the ions moved was, roughly, $(V - CR)/d$. Hence

$$u = \frac{760}{p} \frac{V - CR}{d} u_0,$$

where u_0 is the velocity of the ionic stream moving under 760 mm. pressure and 1 volt per centimetre. Therefore

$$C = Q \times 10^{-6} \times 760\,(V - CR)\,u_0/pd^2. \qquad (a)$$

This equation (since $d^2 = 0\cdot3\,q.p.$) makes the ratio V/CR equal to

$$1 + \frac{1}{4\cdot5\,u_0}, \qquad 1 + \frac{1}{1\cdot2\,u_0}, \qquad 1 + \frac{1}{4\cdot1\,u_0}, \text{ respectively,}$$

in the case of the first three observations of Table III. Now u_0 is probably greater than, and cannot be much less than, unity*; therefore V — CR is substantially less than V. This result has been obtained on the assumption that the current was constant and the field of force undisturbed by the flow of ions. But the conclusion at least indicates that in the actual case CR

* See Sir J. J. Thomson's 'Conduction of Electricity through Gases.'

became comparable to V in the course of the discharge, and the voltage difference of the cylinders sufficiently reduced to account for the small values of Q.

Hence the smaller values of Q observed when a resistance was in the circuit may be attributed to the reduced difference of potential between the electrodes, which permitted a greater amount of recombination to take place.

But it does not follow that when the resistance was absent there was no recombination. For the above equation (*a*) shows that the current, if assumed to be uniform, was throughout of the order of magnitude $10^{-1}u_0$ when $R = 0$, so that it was quite large enough to produce polarisation of the electrodes, involving recombination.

General Conclusion.—The general result of these experiments is to show that the number of pairs of ions generated by an explosion of azoimide is exceedingly small compared with the number of molecules dissociated by the explosion. The observed proportion is so small (always less than 1 to 100,000) as to lead to the conclusion that dissociated atoms do not in general carry electrostatic charges ; for, if in general they are charged, it is difficult to see how recombination could be so complete in such a strong field of force as in the present case—a field which would impart a high velocity to such electrified atoms. The same conclusion can be drawn from the experiments already alluded to on the electrical effects of exploding electrolytic gas in a field of force.*   In fact the latter effects are not so great as the effects of exploding azoimide.†

What then is the explanation of the formation of ions during the explosion ? The explanation is probably to be found in the mutual collisions of the dissociated atoms as they unite in forming the product of the explosion. The energetic nature of those collisions is shown by the evolution of heat. Under favourable conditions of impact, including a sufficiently high relative velocity, ionisation may take place, just as Townsend has shown that a positive ion, which is either of atomic or molecular dimensions, is capable under such conditions of impact of breaking up a molecule which it strikes into ions.‡

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* See also P. J. Kirkby, 'Roy. Soc. Proc.,' 1911, A, vol. 85, where a definite proof is given that separated atoms of oxygen are uncharged.

† A comparison of the two greatest effects observed in exploding HN_3 and $2H_2 + O_2$ makes the number of ions, per gramme-molecule of each gas exploded, just 100 times greater in azoimide than in electrolytic gas. It is possible, however, that the battery used in the experiments upon the latter gas may have been earthed through a resistance (100,000 ohms or less), in which case the electrical effects may have been greater than they were observed to be.

‡ Townsend, 'Ionisation of Gases by Collision,' p. 38.

Lowest Pressure of Explosion.—The lowest pressure at which azoimide was observed to explode in the apparatus described above was 11 mm.   No explosion took place at pressures of 10 mm. or less.   Observations made with different specimens of the gas were very consistent in this respect. Hence 10·5 mm. was very nearly the pressure-limit of explosions.   This limit would probably be lower still ·for pure azoimide.   For, in view of the imperfect evacuation of the oil pump, it cannot be asserted that more than 80 per cent. of the gas at the pressure 10 mm. was azoimide.

In this respect azoimide presents a sharp contrast with electrolytic gas, which does not explode at pressures much below 80 mm.,* a contrast that illustrates the highly explosive nature of azoimide.   This striking difference might, perhaps, be modified if electrolytic gas were exploded when not drier than the azoimide was.   But the contrast in any case would be great, for electrolytic gas was found† to combine under the electric discharge with perfect regularity at the pressure 39 mm., so that even when mixed with water-vapour its pressure of explosion must exceed 39 mm.

It is natural to conclude from these two cases that all explosive gases cease to explode even partially when their pressure is below a certain critical pressure, depending, of course, upon their temperature.   The explanation is probably that the heat radiated from the molecules, formed as the product of the explosion in that region of the gas where the explosion originates, plays an important part in exploding the adjacent portions of the gas, namely, by raising its temperature and thus facilitating its dis-integration by molecular or atomic collisions.   If that is the case, when the pressure is reduced below a certain point, the molecules will be so far apart that the intensity of this radiation, diminishing as the inverse square of the distance, will cease to have the same effect, and the reaction will not be propagated.

It should be added that the least pressure at which explosion occurs seems to depend partly on the apparatus and partly on the manner of starting the explosion.   Thus in one apparatus consisting of two brass discs about 7 cm. in diameter, and insulated from each other by an ebonite ring about 5 mm. thick, the azoimide did not explode by the heating of a platinum wire fixed between the discs until a pressure of over 200 mm. was reached, when the gas exploded with great violence, wrecking the apparatus and destroying the adjacent vessel in which a supply of azoimide had been collected over mercury (G, fig. 1).

Absorption of Azoimide by Phosphorus Pentoxide.—The first efforts to dry

* Haselfoot and Kirkby, *loc. cit.*
† P. J. Kirkby, 'Phil. Mag.,' January, 1905, p. 182.

azoimide over phosphorus pentoxide were not successful. The gas was absorbed as fast as it was admitted to the drying vessel. This effect, however, was greatly diminished by the substitution of fresh phosphorus pentoxide, which was carefully introduced into the drying vessel so as to be as dry as possible. It was found, however, that eventually this substance also absorbed azoimide with great rapidity. It follows that azoimide is absorbed by one of the phosphoric acids, into which P_2O_5 is partly transformed by the absorption of water-vapour, but is not absorbed by pure P_2O_5.

Formation of Crystalline Copper Azoimide on the Sides of the Explosion Chamber.—When the series of explosion experiments was finished and the explosion chamber opened, it was found that part of the gold surface had been attacked. In the part which lay in the direct line of fire from the ignition point the surface was covered with a dark-coloured deposit. The rest of the gold was bright. The small amount of the deposit rendered a quantitative analysis impracticable. A little scraped off the side was found to be transparent and crystalline when examined under the microscope. When held in the flame it exploded with a green-coloured flash. It was apparently not acted on by water, but hydrochloric acid dissolved it. This solution was found to contain azoimide, which was recognised by its characteristic smell and by giving, when distilled into silver nitrate solution, a white explosive precipitate. The solution did not contain gold, but copper in the cupric state was recognised by the ordinary tests. A cupric azoimide is thus formed in the explosion chamber. It seemed surprising that an explosive substance could be formed under such conditions and could survive after a long series of subsequent explosions.

A hydrated cupric salt of azoimide has been obtained by Curtius (the discoverer of azoimide) and Rissom.* It is precipitated on mixing a solution of a salt of azoimide with a solution of a cupric salt, and has a reddish-brown colour. Curtius and Rissom describe it as crystalline and highly explosive, even when moist, " eines der gefährlichst zu handhabenden Salze des Stickstoffwasserstoffs." It was not obtained by them free from water, even when kept in a desiccator.

Azoimide does not attack gold, nor when dried by calcium chloride does it appreciably attack clean brass. But in presence of air and water-vapour it attacks brass with the formation, after a few hours, of a black deposit which explodes with a green flash and dissolves in ammonia with a blue colour. This deposit is undoubtedly a cupric azoimide, but, as formed in this way, it is not crystalline and transparent, but amorphous and opaque, very different from the deposit in the explosion chamber. Copper is also

* 'Journ. Pr. Chem.' (2), vol. 58, p. 261.

attacked by moist azoimide vapour, giving the same black deposit. Zinc also is not attacked by dry azoimide, but in the moist gas it gives a white deposit which explodes with a bluish-white flash.

We have now to consider how the cupric azoimide comes to be formed in the explosion chamber. In the first place, it is unlikely that the formation is due to the action of the azoimide before explosion, since azoimide does not attack gold and hardly attacks brass when dry.* Nor is it likely that the gold helped the azoimide to attack the brass; otherwise the whole of the gold surface would have been attacked, whereas a considerable portion was bright and free from deposit. Moreover, no diminution in volume was noticed when the charges of azoimide were admitted into the explosion chamber. For the same reasons the explanation is precluded that the gold coating was ripped off by the first explosions, and that the azoimide then attacked the exposed brass. The deposit, moreover, was crystalline, while that formed slowly on brass by exposure to moist azoimide was found to be amorphous, though it is, perhaps, possible that an amorphous deposit formed in the first instance might be hammered into crystals by a series of explosions.

It seems, on the whole, most probable that the copper azoimide was formed during the actual explosions, and itself escaped explosion owing to its comparative stability, and to the fact that it was in contact with metal which would easily absorb the energy of subsequent explosions. From the above description given by Curtius and Rissom of the hydrated copper salt, it would appear that the salt obtained by explosion is much more stable than the one they observed, and this may be due to its being the anhydrous salt.

If, then, copper azoimide is formed by the explosions, it follows that a fair degree of stability belongs to the group N_3. Hence it is not unlikely that the first stage of the explosion is to break up HN_3 into H and N_3, some of the N_3 groups escaping further decomposition by being driven through the gold into combination with the copper. It might be supposed that the N_3 groups, being the same as the electrolytic chemical ions, were the cause of the electrical effect. But this is improbable, since the quantity of copper azoimide formed, though small, was much larger than could be accounted for by the very slight electrical effect on the assumption that every N_3 carried the atomic charge.

* An absorption of azoimide was noticed by us when a brass explosion chamber was used, instead of the gilded one. This absorption was, no doubt, due to the presence of oxide or other impurity on the brass. No absorption was ever noticed with the gilded brass even after many explosions had been made with it, when some of the gold surface may have been torn off.